

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification<sup>5</sup> :</b> <b>C08L 23/16, 23/08, 33/08</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 94/12569</b> <b>(43) International Publication Date:</b> 9 June 1994 (09.06.94)
<b>(21) International Application Number:</b> PCT/US93/11456 <b>(22) International Filing Date:</b> 24 November 1993 (24.11.93)  <b>(30) Priority Data:</b> 07/983,915 1 December 1992 (01.12.92) US  <b>(71) Applicant:</b> CHEVRON RESEARCH AND TECHNOLOGY COMPANY [US/US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US).  <b>(72) Inventor:</b> GALANTE, Nicholas, R.; 708 Sherrell Street, Orange, TX 77630 (US).  <b>(74) Agents:</b> HOLLAND, Charles, D. et al.; Chevron Corporation, Law Department, P.O. Box 7141, San Francisco, CA 94120-7141 (US).		<b>(81) Designated States:</b> AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> POLYMER BLENDS CONTAINING PROPYLENE-ETHYLENE COPOLYMER AND ETHYLENE-ALKYL ACRYLATE COPOLYMER  <b>(57) Abstract</b>  Compositions are provided comprising a propylene-ethylene copolymer containing about 1 to about 7 weight percent ethylene and an ethylene-alkyl acrylate copolymer containing at least about 20 weight percent ethylene, wherein the composition contains about 10 to 25 weight percent alkyl acrylate, based on the combined weight of propylene-ethylene copolymer and ethylene-alkyl acrylate copolymer. Films made from these compositions have good RF sealing properties, as well as good flexibility at low temperatures.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Larvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

01 POLYMER BLENDS CONTAINING PROPYLENE-ETHYLENE COPOLYMER  
02 AND ETHYLENE-ALKYL ACRYLATE COPOLYMER  
03

04 FIELD OF THE INVENTION  
05

06 The present invention relates to polymer blends comprising a  
07 propylene-ethylene copolymer and an ethylene-alkyl acrylate  
08 copolymer.  
09

10 BACKGROUND OF THE INVENTION  
11

12 Polymer blends containing propylene polymers and ethylene  
13 copolymers are known. For example, U. S. Patent  
14 No. 3,433,573, issued March 18, 1969 to Holladay et al.,  
15 discloses compositions containing blends of 5 to 95% by  
16 weight of a propylene polymer containing a major amount of  
17 propylene and 95 to 5% by weight of a copolymer of ethylene  
18 with a polar monomer such as vinyl acetate, methyl  
19 methacrylate, vinylidene carbonate, alkyl acrylates, vinyl  
20 halides and vinylidene halides. However, the only ethylene  
21 copolymer used in the examples is an ethylene-vinyl acetate  
22 copolymer. These compositions are said to be useful in  
23 fibers, films and molded articles of improved dyeability and  
24 low temperature characteristics.  
25

26 U. S. Patent No. 3,555,110, issued to McConnell et al. on  
27 January 12, 1971, discloses that ethylene copolymers such as  
28 ethylene/alkyl acrylate, ethylene/aryl acrylate and  
29 ethylene/alkenyl carboxylate copolymers are compatible with  
30 alpha-monoolefin block polymers such as propylene/ethylene  
31 polymers having from about 50% to 99% by weight of  
32 polypropylene segment in the polymer chain. Objects  
33 prepared from these polymer blends are said to have  
34

- 2 -

01 excellent clarity, improved low temperature properties and  
02 good impact strength at low temperature.

03

04 U. S. Patent No. 4,774,277, issued on September 27, 1988 to  
05 Janac et al., discloses compositions useful in the  
06 preparation of film which is said to be soft and have high  
07 tensile, tear and impact strength. The compositions contain  
08 polyolefin plastics blended with an elastomeric plasticizer.  
09 The disclosed polyolefin plastics are polypropylene,  
10 polypropylene reactor copolymer, polybutylene, linear  
11 low density polyethylene, high density polyethylene or  
12 mixtures thereof. The elastomeric plasticizer contains  
13 (1) polyethylene or a copolymer of ethylene and an  
14 unsaturated ester of a lower carboxylic acid, (2) olefin  
15 elastomer, such as copolymers of ethylene with higher  
16 alpha-olefins such as propylene containing about 30-90  
17 weight percent ethylene, and (3) a hydrocarbon oil.

18

19 U. S. Patent No. 4,835,218, issued May 30, 1989 to  
20 Yoshimura et al., discloses a composition for shrinkable  
21 film which is said to have good heat sealability,  
22 transparency, strength, and low temperature quick shrinking  
23 properties. The composition contains specific combinations  
24 of (A), (B) and (C), i.e., the combinations of (A)+(B),  
25 (B)+(C), and (A)+(B)+(C), wherein (A) is non-rigid  
26 polyolefin resins such as ethylene-vinyl acetate, (B) is an  
27 elastomer comprising a specific ethylene-alpha-olefin  
28 copolymer and an elastomer consisting of block copolymer  
29 having at least one monovinyl substituted aromatic  
30 hydrocarbon polymer block and at least one polyolefin  
31 polymer block selected from at least one saturated polymer  
32 or unsaturated polymer made from mainly aliphatic conjugate  
33 diene derivative, and (C) is rigid polyolefin resins such as  
34 polypropylene.

- 3 -

SUMMARY OF THE INVENTION

01

02

03 In accordance with the present invention, there is provided  
04 a composition comprising:

05

06 A. a propylene-ethylene copolymer comprising about 1  
07 to about 7 weight percent ethylene; and

08

09 B. an ethylene-alkyl acrylate copolymer comprising at  
10 least about 20 weight percent alkyl acrylate,

11

12 wherein the percent by weight of alkyl acrylate, based on  
13 the weight of A and B, is from about 10 to about 25.

14

15 Also provided in accordance with the present invention is a  
16 film made from a composition comprising:

17

18 A. a propylene-ethylene copolymer comprising about 1  
19 to about 7 weight percent ethylene; and

20

21 B. an ethylene-alkyl acrylate copolymer comprising at  
22 least about 20 weight percent alkyl acrylate,

23

24 wherein the percent by weight of alkyl acrylate, based on  
25 the weight of A and B, is from about 10 to about 25.

26

27 Among other factors, the present invention is based upon the  
28 discovery that films made from the compositions of this  
29 invention are RF sealable when a signal having about 27.2  
30 MHz frequency, and about 1.1 KW/inch<sup>2</sup> power is applied for  
31 about 1.5 seconds. In comparison, films made from the  
32 propylene-ethylene copolymer alone will not RF seal.

33

34

01                    DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

02

03    The propylene-ethylene copolymers useful in the compositions  
04    of this invention comprise copolymers of propylene and  
05    ethylene in which the ethylene comprises about 1 to about 7,  
06    preferably about 1 to about 5, more preferably about 2 to  
07    about 2.5 weight percent of the copolymer, based on the  
08    combined weight of propylene and ethylene. These propylene-  
09    ethylene copolymers may also contain minor amounts of at  
10    least one additional monomer, such as butene, though this  
11    additional monomer(s) is not necessary.

12

13    The propylene-ethylene copolymers of this invention are  
14    random copolymers. That is, the propylene and ethylene are  
15    randomly distributed along the polymer chain, as opposed to  
16    being present in block copolymer form.

17

18    Examples of the propylene-ethylene copolymers useful in this  
19    invention include the copolymer designated SA861 having a  
20    melt flow rate (as measured by ASTM D12386) of about 6 and  
21    an ethylene content of about 2.2 weight percent, and the  
22    copolymer designated KT011P, both of which are sold by  
23    Himont Inc. The preferred propylene-ethylene copolymer is  
24    SA861.

25

26    The ethylene-alkyl acrylate copolymers which form part of  
27    the compositions of this invention are copolymers of  
28    ethylene and one or more alkyl acrylates. Examples of the  
29    alkyl acrylates include, but are not limited to, acrylic  
30    esters of linear, branched or cyclic alcohols having 1-28  
31    carbon atoms. The alkyl acrylate esters are exemplified by,  
32    but not limited to, methyl acrylate, ethyl acrylate and  
33    butyl acrylate, with methyl acrylate and butyl acrylate  
34    being preferred.

- 5 -

01 One preferred group of ethylene-ester copolymers are  
02 ethylene-alkyl acrylate copolymers which have high melting  
03 points. These ethylene-alkyl acrylate copolymers have an  
04 alkyl acrylate content of X weight percent, X being 20 or  
05 more and being based on the total weight of ethylene and  
06 alkyl acrylate in the copolymer, the copolymer having an  
07 average melt-point temperature equal to or greater than the  
08 value obtained from the expression:

09

$$10 \quad \text{temperature (deg F)} = 238 - 2.16X.$$

11

12 One example of these copolymers are ethylene-methyl acrylate  
13 copolymers having a methyl acrylate content of Y weight  
14 percent, Y being 20 or more and being based on the total  
15 weight of ethylene and methyl acrylate in the copolymer, the  
16 copolymer having an average melt-point temperature equal to  
17 or greater than the value obtained from the expression:

18

$$19 \quad \text{temperature (deg F)} = 248 - 2.9Y.$$

20

21 Another example of these copolymers are ethylene-butyl  
22 acrylate copolymers having a butyl acrylate content of Z  
23 weight percent, Z being 20 or more and based on the total  
24 weight of ethylene and butyl acrylate in the copolymer, the  
25 copolymer having an average melt-point temperature equal to  
26 or greater than the value obtained from the expression:

27

$$28 \quad \text{temperature (deg F)} = 240 - 2.1Z.$$

29

30 These high melt point ethylene-alkyl acrylate copolymers can  
31 be made by a process comprising:

32

33

34

- 6 -

- 01       A.    feeding overall an amount by weight, A, of alkyl  
02           acrylate and an amount by weight, E, of ethylene to  
03           a multi-zoned polymerization reactor;  
04  
05       B.    introducing an effective amount of an initiator and  
06           at least a portion,  $E_1$ , of the total amount of  
07           ethylene into a first reaction zone of the reactor;  
08  
09       C.    concurrently introducing a portion,  $A_1$ , of alkyl  
10           acrylate to said first reaction zone such that (1)  
11           greater than about 55% of the overall amount of  
12           alkyl acrylate is introduced into said first  
13           reaction zone, (2) the amount,  $A_1$ , of alkyl  
14           acrylate fed to said first reaction zone is greater  
15           than the total amount of alkyl acrylate fed to all  
16           subsequent reaction zones, and (3) the ratio of  $A_1$   
17           to  $E_1$  in said first reaction zone is equal to or  
18           greater than the ratio of A to E for the reactor  
19           overall; and  
20  
21       D.    feeding any remaining portions of initiator,  
22           ethylene and alkyl acrylate to a subsequent  
23           reaction zone or zones.  
24

25       Preferably, the ratio of  $E_1$  to E is between about 0.25 and  
26       about 0.75, more preferably about 0.50, and the ratio of  $A_1$   
27       to  $E_1$  is preferably greater than 1.2, more preferably  
28       greater than 1.4 times the ratio of A to E.  
29

30       Another process for the preparation of these high-melting  
31       ethylene-alkyl acrylate copolymers comprises introducing to  
32       a first reaction zone in a multi-zone reactor, initiator,  
33       ethylene and a quantity of an alkyl acrylate which is (1) in  
34       excess of 50% of the amount of alkyl acrylate fed overall to



01 the reactor and (2) greater than the total amount of alkyl  
02 acrylate fed to all subsequent reaction zones, said quantity  
03 of alkyl acrylate being effective to increase the average  
04 melt-point temperature of said copolymers at least about 8°F  
05 over the melt-point temperature of a copolymer having the  
06 same alkyl acrylate content by weight as said produced  
07 copolymer and made by introducing about 50% of the alkyl  
08 acrylate fed overall to the reactor to said first reaction  
09 zone and about 50% of the ethylene fed overall to the  
10 reactor to said first reaction zone.

11  
12 These processes are described in greater detail below. As  
13 used herein, the following terms have the following  
14 meanings:

- 15
- 16 1. "A" is used herein to denote the total amount by  
17 weight of alkyl acrylate fed to the reactor.  
18
  - 19 2. "A<sub>1</sub>" is used to denote the portion of the amount A  
20 which is fed to first reaction zone in said  
21 reactor.  
22
  - 23 3. "E" is used to denote the total amount by weight  
24 ethylene fed to the reactor.  
25
  - 26 4. "E<sub>1</sub>" is used to denote the portion of the amount E  
27 which is fed to the first reaction zone.  
28
- 29 One appropriate measure of these amounts is pounds (mass).  
30
- 31 5. "First reaction zone" refers to the area in a  
32 reactor where ethylene and alkyl acrylate come into  
33 contact under polymerization conditions, and a  
34 substantial amount of polymerization occurs.

- 8 -

01           However, the "first reaction zone" need not be the  
02           first in a sequence of zones in the reactor. For  
03           example, ethylene and/or alkyl acrylate could be  
04           introduced into a zone of the reactor prior to the  
05           "first reaction zone," but if no significant  
06           polymerization occurs in this prior zone (e.g.,  
07           less than about 5% of the total reaction takes  
08           place), this zone is not considered herein to be  
09           the "first reaction zone."  
10

11           6. "Reaction zone" refers to an area within a single  
12           reaction vessel in which polymerization of the  
13           ethylene and/or alkyl acrylate takes place.  
14           Typically, the "reaction zone" is a portion of a  
15           single reaction vessel which is segregated from  
16           other areas of the same reaction vessel. This  
17           segregation can be accomplished by physical  
18           barriers (such as baffles and the like), or other  
19           suitable means (such as the mixing patterns within  
20           the reaction vessel). As used herein, the term  
21           "reaction zone" also includes areas in separate,  
22           multiple reaction vessels where polymerization  
23           occurs. Although multiple reactors may be used, in  
24           one preferred embodiment, the process uses a  
25           multi-zoned, high-pressure autoclave reactor. A  
26           4-zone reaction system is preferred and is  
27           exemplified in Figure 1, although additional zones,  
28           such as six, or fewer zones, such as two zones, can  
29           be used.  
30

31           This process starts by feeding ethylene gas under high  
32           pressure to the reactor.  
33  
34

- 9 -

01 Preferably, the ethylene is fed into the top of the reactor  
02 and into Reaction Zone 1. The reactor zones are numbered  
03 from top to bottom. Alkyl acrylate monomer is fed to the  
04 reactor in an overall amount by weight of A pounds, and is  
05 divided to feed selected zones. In one embodiment, Zone 1  
06 is fed  $A_1$  pounds, and Zone 2 is fed  $(A - A_1)$  pounds.

07

08 In a continuous process the total feed of alkyl acrylate  
09 relative to the total ethylene feed determines the alkyl  
10 acrylate content of the final copolymer. A copolymer  
11 containing 20 wt% alkyl acrylate has a smaller total feed  
12 ratio of alkyl acrylate to ethylene (A/E) than a copolymer  
13 containing 30 wt% alkyl acrylate. To achieve the desired  
14 product, an overall A/E feed ratio is chosen and generally  
15 maintained throughout a production run, although the ratio  
16 A/E can be varied over time to produce copolymers containing  
17 different weight percentages of alkyl acrylate.

18

19 The ratio of the amount by weight of alkyl acrylate monomer  
20 to the amount by weight of ethylene monomer in a first  
21 reaction zone ( $A_1/E_1$ ) relative to the ratio of the overall  
22 amount by weight of alkyl acrylate monomer to the overall  
23 amount by weight of ethylene monomer (A/E) is critical to  
24 obtain the improved properties of this type of  
25 ethylene-alkyl acrylate copolymer. If the ratio  $A_1/E_1$  is  
26 equal to or greater than the overall ratio A/E required to  
27 make the ethylene-alkyl acrylate copolymer, and if  $A_1$  is at  
28 least about 55% of A and exceeds the amount of alkyl  
29 acrylate, if any, fed to all subsequent zones, then the  
30 melt-point temperature of the copolymer is significantly  
31 increased over conventional copolymers having the same alkyl  
32 acrylate content.

33

34

- 10 -

01 In one preferred embodiment of this process, the ethylene,  
02 E, fed to the 4-zone is divided so that  $E_1$ , the amount of  
03 ethylene in a first reaction zone (in this case, Zone 1), is  
04 about 25% to 75%, and, more preferably, about 50%, of E.  
05 About 75% to 25%, and more preferably about half, of the  
06 ethylene monomer is fed into Zone 2.  $A_1$  is controlled such  
07 that  $A_1$  is greater than 55%, preferably at least 70%, of A  
08 and such that the ratio  $A_1/E_1$  is equal to or greater than  
09 the ratio of A/E. Preferably, the ratio  $A_1/E_1$  is greater  
10 than about 1.4, and more preferably is in excess of 1.8,  
11 times the ratio A/E. Most preferably, all of the alkyl  
12 acrylate is added to the first reaction zone in order to  
13 attain ethylene-alkyl acrylate copolymers having the highest  
14 melt-point temperatures.

15

16 The preferred temperature in the first reaction zone is  
17 about 300°F to 450°F, and more preferably is about 325°F to  
18 425°F.

19

20 High pressures are preferred when producing these high  
21 melting ethylene-alkyl acrylate copolymers. The reaction  
22 zone pressure preferably is about 10,000 to about 40,000  
23 psig, more preferably about 15,000 to about 35,000 psig, and  
24 most preferably is about 20,000 to about 30,000 psig.

25

26 A free radical initiator is preferably used to catalyze the  
27 polymerization. The initiator can be added into any zones  
28 where polymerization is desired. The initiator preferably  
29 is fed into at least the first reaction zone in a sufficient  
30 amount and rate whereby the temperature of the liquid phase  
31 in the reaction zone is controlled in the range specified  
32 above.

33

34

- 11 -

01 The initiator may be added to the reaction zone(s) in any  
02 suitable manner. Generally, it is dissolved in a suitable  
03 solvent, typically a hydrocarbon, and injected into the  
04 zone(s). Normally, the initiator and alkyl acrylate are  
05 simultaneously injected into the reaction zone(s), though  
06 this is not essential. In a preferred embodiment, the  
07 initiator and alkyl acrylate are simultaneously injected  
08 into the reaction zone via concentric tubes, one carrying  
09 the initiator and the other carrying the alkyl acrylate.

10

11 Examples of initiators include, peroxides such as lauroyl  
12 peroxide, t-butyl perbenzoate, t-butyl peroxyphthalate and  
13 di-t-butyl peroxide. A preferred initiator is t-butyl  
14 peroxyphthalate. Typically, the initiator is dissolved in a  
15 liquid hydrocarbon such as hexane or mineral oil.

16

17 In preparing the high-melting ethylene-alkyl acrylate  
18 copolymers, is desirable to add an oxygen scavenging  
19 compound to the reaction mixture. Phenolic compounds are  
20 useful in this regard. These phenolic compounds include  
21 2,6-di-t-butyl-4-methylphenol (BHT) and 2,6-  
22 di-t-butyl-4-ethylphenol (BHEB). These compounds are well  
23 known in the art; see U.S. Patent No. 3,941,747, issued  
24 March 2, 1976 to Roth et al., which is incorporated herein  
25 by reference. A preferred compound is BHEB. The addition  
26 of the oxygen scavenging compound is at a rate such that the  
27 concentration of the compound is preferably 0.01 to 0.5,  
28 more preferably 0.05 to 0.10 wt%, of the total copolymer  
29 produced.

30

31 The reaction mixture is agitated within the first reaction  
32 zone to produce both radial and longitudinal mixing.  
33 Preferably a substantially uniform reaction temperature is  
34 maintained.

- 12 -

01 The reaction mixture proceeds from the first reaction zone  
02 into a second reaction zone. The reaction mixture in the  
03 second zone preferably is agitated to produce good radial  
04 and longitudinal mixing. Preferably, the remaining alkyl  
05 acrylate monomer, ethylene and additional free radical  
06 initiator are introduced into the second reaction zone.  
07 Also preferably, the three components are added separately.  
08 The initiator is fed into the second reaction zone in a  
09 sufficient amount and rate whereby the temperature of the  
10 liquid phase in the final reaction zone is controlled to  
11 about 350°F to 450°F, more preferably to about 350°F to  
12 425°F, and most preferably 375°F to 425°F.

13

14 Preferably, there are one or more reaction zones after the  
15 second reaction zone which are used to further polymerize  
16 the ethylene and alkyl acrylate monomers. The reaction  
17 mixture is removed from the end of Zone 2 (the second  
18 reaction zone, in this case) and introduced into, e.g., two  
19 additional reaction zones, where the mixture is agitated to  
20 produce both radial and end-to-end mixing.

21

22 The amount of alkyl acrylate in the compositions of the  
23 present invention has been found to be critical in two  
24 respects. First, the overall amount of alkyl acrylate in  
25 the composition must be from about 10 to about 25 percent by  
26 weight of the composition, based on the combined weight of  
27 the propylene-ethylene copolymer and ethylene-alkyl acrylate  
28 copolymer. However, it has been found that it is not enough  
29 simply to provide compositions with this amount of alkyl  
30 acrylate in order to make films which have good RF sealing  
31 properties. Instead, it has been found that the ethylene-  
32 alkyl acrylate copolymer used in the compositions must  
33 contain a minimum amount of alkyl acrylate, i.e., at least  
34 about 20 weight percent alkyl acrylate. Thus, it has been

- 13 -

01 found that it is not sufficient to merely provide a  
02 composition containing a minimum amount of alkyl acrylate  
03 (as by making a composition containing a large amount of  
04 ethylene-alkyl acrylate copolymer which, in turn, contains a  
05 very small amount of alkyl acrylate), but rather the alkyl  
06 acrylate must be concentrated in an ethylene-alkyl acrylate  
07 copolymer containing relatively large amounts of alkyl  
08 acrylate (e.g., 20 weight percent or more).

09  
10 It is apparent from the foregoing discussion of the amount  
11 of alkyl acrylate in both the ethylene-alkyl acrylate  
12 copolymer and the overall composition that the relative  
13 proportions of the propylene-ethylene copolymer and  
14 ethylene-alkyl acrylate copolymer will depend upon the alkyl  
15 acrylate content of the particular ethylene-alkyl acrylate  
16 copolymer employed. Thus, for example, more of an ethylene-  
17 alkyl acrylate copolymer containing about 20 weight percent  
18 alkyl acrylate would be necessary to satisfy the requirement  
19 that the overall composition contain about 10 to 25 weight  
20 percent alkyl acrylate than would be required for an  
21 ethylene-alkyl acrylate copolymer containing, e.g., 30  
22 weight percent alkyl acrylate. Typically, the compositions  
23 of this invention contain at least about 20 weight percent,  
24 based on the combined weight of the propylene-ethylene  
25 copolymer and ethylene-alkyl acrylate copolymer, of  
26 propylene-ethylene copolymer, with the balance being  
27 ethylene-alkyl acrylate copolymer containing sufficient  
28 alkyl acrylate to satisfy the requirement of about 10 to  
29 about 25 weight percent alkyl acrylate, based on the  
30 combined weight of the propylene-ethylene copolymer and  
31 ethylene-alkyl acrylate copolymer.

32  
33 In one preferred embodiment of this invention, compositions  
34 are provided comprising a propylene-ethylene copolymer and

- 14 -

01 an ethylene-alkyl acrylate copolymer wherein the ethylene-  
02 alkyl acrylate copolymer comprises about 20 to about 25  
03 weight percent alkyl acrylate, and the percent by weight of  
04 alkyl acrylate, based on the combined weight of the  
05 propylene-ethylene copolymer and ethylene-alkyl acrylate  
06 copolymer, is at least about 15. In another preferred  
07 embodiment, the present invention provides such compositions  
08 wherein the alkyl acrylate content of the propylene-ethylene  
09 copolymer is about 25 weight percent and the weight percent  
10 alkyl acrylate, based on the weight of propylene-ethylene  
11 copolymer and ethylene-alkyl acrylate copolymer, is at least  
12 about 10.

13  
14 The compositions of the present invention may be made simply  
15 by blending the propylene-ethylene and ethylene-alkyl  
16 acrylate copolymers until a uniform mixture is achieved.  
17 This may be accomplished by techniques well known in the  
18 polymer arts, such as by blending in mechanical mixers like  
19 a Brabender Plasticorder, a roll mill, a single or multiple  
20 screw extruder or any of the other well-known mechanical  
21 mixing equipment normally used in the mixing, compounding,  
22 processing or fabrication of low or high molecular weight  
23 thermoplastic, elastomeric or thermosetting polymers or  
24 mixtures thereof. Preferably, the mixing is conducted at a  
25 temperature high enough for the propylene-ethylene copolymer  
26 and ethylene-alkyl acrylate copolymer to be in a deformable,  
27 e.g., molten, state, but low enough that the polymers are  
28 not degraded during mixing. A typical mixing temperature  
29 would be in the range of from about 400°F to about 450°F.

30  
31 Likewise, the compositions of this invention may be formed  
32 into films by a variety of techniques known in the film  
33 making art. One preferred manner of making films from the  
34 compositions of this invention is by standard blown film



- 15 -

01 extrusion techniques, although conventional cast film  
02 extrusion, sheet extrusion and calendaring techniques may be  
03 used as well.

04

05 When the compositions of this invention are made into thin  
06 films, such as films which are 4 mils thick, the films have  
07 several beneficial properties. First, the films are RF  
08 sealable using lower frequencies and less power than, for  
09 example, films made from blends of polypropylene  
10 (homopolymer) and an ethylene-alkyl acrylate copolymer (see  
11 Table I below). These 4 mil films provide excellent RF  
12 seals at about 27.2 MHz frequency and about 1.1 KW/inch<sup>2</sup>  
13 power for about 1.5 seconds, as opposed to the unsealable  
14 (by RF sealing) films made from a polypropylene  
15 homopolymer/ethylene-alkyl acrylate copolymer blend.

16

17 In addition, the 4 mil films have excellent flexibility,  
18 especially at low temperatures. This is especially useful  
19 in applications, such as blood bags, where the film will be  
20 subjected to extremely low temperatures (e.g., -35°C Red  
21 Cross Standard), yet must remain flexible.

22

23 The films of this invention also possess other good  
24 properties, such as optical and physical properties. For  
25 example, the films of this invention have about 20% haze,  
26 tensile strength greater than 3,300 psi and greater than  
27 700% elongation. In addition, the films of this invention  
28 are typically autoclavable at 120°C for 0.5 hour without  
29 deleterious effects.

30

31 Presently, the standard bags for storing blood are made from  
32 poly(vinyl chloride). These PVC bags, however, can crack  
33 and break at the very low temperatures at which blood is  
34 typically stored. Also, the PVC used to make these blood

- 16 -

01 bags has a density of about 1.26-1.3, and the PVC film used  
02 to make the blood bags is about 14 mils thick. In contrast,  
03 the compositions of the present invention have a density of  
04 only about 0.93, representing a weight savings of about 30%  
05 compared to PVC.

06

07 The compositions of this invention also have advantages over  
08 compositions containing polypropylene (homopolymer) and  
09 ethylene-alkyl acrylate copolymers ("PP/EAA") and  
10 compositions containing polypropylene (homopolymer) and  
11 ethylene-vinyl acetate copolymer ("PP/EVA"). For example,  
12 films made from the PP/EAA compositions do not RF seal as  
13 well as the compositions of this invention. The  
14 compositions of this invention also contain fewer  
15 extractables than do the PP/EVA compositions, and they  
16 provide films with better clarity than the PP/EVA  
17 compositions. In addition, residual vinyl acetate in PP/EVA  
18 blends can cause a pH shift in the contents (e.g., blood,  
19 plasma, etc.) of bags made from such blends.

20

21 The present invention is illustrated by the following  
22 examples, which are not intended to be limiting on its scope  
23 in any way.

24

25

26

27

28

29

30

31

32

33

34

- 17 -

## EXAMPLE 1

01

02

03 The blends shown in Table I below were made, each in turn,  
04 in a ZSK-40 40mm Werner Pfleiderer twin screw compounder.  
05 Operating conditions for the compounder were as follows:

06

07	Screw speed (RPM)	350
08	Torque (%)	60-75
09	Throughput (pph)	200
10	Die pressure (psi)	260-280
11	Vacuum (inches)	27
12	Melt temperature (°C)	223
13	Barrel temperatures (°C)	
14	Zone 1	190
15	Zone 2	200
16	Zone 3	200
17	Zone 4	200
18	Zone 5	200
19	Zone 6	210
20	Zone 7	210

21

22

23

24

25

26

27

28

29

30

31

32

33

34

- 18 -

01  
02  
03  
04  
05  
06  
07  
08  
09  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34

TABLE I												
BLEND COMPOSITIONS												
BLEND COMPONENT <sup>1</sup>	BLEND NO.											
	1	2	3	4	5	6	7	A	B	C	D	E
Propylene-ethylene copolymer	20	40	20	40	20	40	60	60	60			
Polypropylene										20	40	60
EMAC (20% MA, M.I. = 2)			80	60	80	60	40		40			
EMAC (20% MA, M.I. = 0.5)	80	60						40		80	60	40
EMAC (27% MA, M.I. = 2)												
Methyl acrylate content wt. % <sup>2</sup>	16	12	16	12	22	16	11	8	8	16	12	8

<sup>1</sup> Numbers indicate weight percent.<sup>2</sup> Weight percent of methyl acrylate based on total blend weight.

## EXAMPLE 3

Blown films were made by conventional techniques using each in turn the blends described in Table I above. The films were 4 mils thick. The RF sealing properties of these films were tested with the results shown in Table II below.

- 19 -

01  
02  
03  
04  
05  
06  
07  
08  
09  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34

TABLE II												
RF SEAL PROPERTIES												
RF SEAL CONDITIONS <sup>a</sup>	FILM FROM BLEND NO.											
	1	2	3	4	5	6	7	A	B	C	D	E
RF Seal, Preheat time, sec.	0.7	WNS <sup>b</sup>	0.7	WNS	0.5	0.7	0.7	WNS	WNS	0.5	WNS	WNS
RF Seal, Weld time, sec.	1.2	WNS	1.5	WNS	0.5	1.5	1.7	WNS	WNS	1.7	WNS	WNS
RF Seal, Dwell time, sec.	1.0	WNS	1.0	WNS	2.0	1.0	1.0	WNS	WNS	2.0	WNS	WNS
RF Seal, Cycle time, sec.	2.2	WNS	2.5	WNS	2.5	2.5	2.7	WNS	WNS	3.7	WNS	WNS

<sup>a</sup> 27.2 MHz, 12.5 KW sealing unit at 20% power, 3 inch annular die (2.22 inch<sup>2</sup> of sealing area), 0.026 inch NEMA XXXP buffer, 100 psi air pressure, ambient (unheated die).

<sup>b</sup> WNS indicates that film would not seal.

The film properties of these films were also tested, with the results indicated in Table III below.

TABLE III

	1	2	3	4	5	6	7	A	B	C	D	E
Haze, %	12	17	22	16	27	24	19	16	13	18	27	32
Gloss	61	47	61	51	42	49	49	43	51	41	36	31
Clarity, %	1	0	1	0	0	0	0	0	0	0	0	0
MD Tensile Strength, psi	4000	4800	3300	4500	2500	3700	3400	4900	5000	3800	5000	4900
TD Tensile Strength, psi	3900	4300	3000	4500	2000	3400	3300	4100	4400	3700	4000	4000
MD Tensile Yield, psi	---	1800	---	2300	---	1500	1400	2400	2600	---	2200	2300
TD Tensile Yield, psi	---	1600	---	2200	---	1300	1300	2300	1700	---	1900	2000
MD Elongation, %	655	695	625	690	740	730	705	730	730	625	720	680
TD Elongation, %	705	700	630	720	700	810	720	695	735	645	690	680
MD Elmendorf Tear, gm/mil	200	150	300	80	280	160	170	60	80	210	80	80
TD Elmendorf Tear, gm/mil	230	330	190	60	160	210	190	70	50	190	110	120
MD 1% Secant Modulus, mpsi	20	46	23	64	19	41	41	66	77	26	64	64
TD 1% Secant Modulus, mpsi	17	40	16	60	8	31	29	63	68	21	55	55
Coefficient of Friction	>2.00	1.47	1.94	0.87	>2.00	1.50	1.45	0.94	0.42	1.70	0.96	0.90

The cast film is oriented in one direction as it is made. MD refers to the direction of orientation; TD refers to the direction traverse to the direction of orientation.

- 21 -

01

02 WHAT IS CLAIMED IS:

03

04 1. A composition comprising:

05

06 A. a propylene-ethylene copolymer comprising about 1 to  
07 about 7 weight percent ethylene; and

08

09 B. an ethylene-alkyl acrylate copolymer comprising at  
10 least about 20 weight percent alkyl acrylate,

11

12 wherein the percent by weight of alkyl acrylate, based  
13 on the weight of A and B, is from about 10 to about 25.

14

15 2. The composition of Claim 1 wherein the propylene-  
16 ethylene copolymer comprises about 1 to about 5 weight  
17 percent ethylene.

18

19 3. The composition of Claim 1 wherein the propylene-  
20 ethylene copolymer comprises about 2 to about 2.5 weight  
21 percent ethylene.

22

23 4. The composition of Claim 1 wherein the propylene-  
24 ethylene copolymer comprises about 2.2 weight percent  
25 ethylene.

26

27 5. The composition of Claim 1 wherein the ethylene-alkyl  
28 acrylate copolymer comprises about 20 to about 25 weight  
29 percent alkyl acrylate, and the percent by weight of  
30 alkyl acrylate based on the weight of A and B is at  
31 least about 15.

32

33 6. The composition of Claim 1 wherein the ethylene-alkyl  
34 acrylate copolymer comprises about 25 weight percent

- 22 -

- 01 alkyl acrylate, and the percent by weight of alkyl  
02 acrylate based on the weight of A and B is at least  
03 about 10.  
04
- 05 7. The composition of Claim 1 wherein the ethylene-alkyl  
06 acrylate copolymer is an ethylene-methyl acrylate  
07 copolymer.  
08
- 09 8. The composition of Claim 3 wherein the ethylene-alkyl  
10 acrylate copolymer is an ethylene-methyl acrylate  
11 copolymer.  
12
- 13 9. The composition of Claim 5 wherein the ethylene-alkyl  
14 acrylate copolymer is an ethylene-methyl acrylate  
15 copolymer.  
16
- 17 10. The composition of Claim 6 wherein the ethylene-alkyl  
18 acrylate copolymer is an ethylene-methyl acrylate  
19 copolymer.  
20
- 21 11. The composition of Claim 1 wherein the ethylene-alkyl  
22 acrylate copolymer has an average melt-point temperature  
23 equal to or greater than the value obtained from the  
24 expression:  
25
- 26 
$$\text{temperature (deg F)} = 238 - 2.16X$$
  
27
- 28 wherein X is the alkyl acrylate content of the ethylene-  
29 alkyl acrylate copolymer.  
30
- 31 12. The composition of Claim 8 wherein the ethylene-alkyl  
32 acrylate copolymer is an ethylene-methyl acrylate  
33 copolymer having an average melt-point temperature equal  
34



- 23 -

01 to or greater than the value obtained from the  
02 expression:

03

04  $\text{temperature (deg F)} = 248 - 2.9Y$

05

06 wherein Y is the methyl acrylate content of the  
07 ethylene-methyl acrylate copolymer.

08

09 13. A film made from a composition comprising:

10

11 A. a propylene-ethylene copolymer comprising about 1 to  
12 about 7 weight percent ethylene; and

13

14 B. an ethylene-alkyl acrylate copolymer comprising at  
15 least about 20 weight percent alkyl acrylate,

16

17 wherein the percent by weight of alkyl acrylate, based  
18 on the weight of A and B, is from about 10 to about 25.

19

20 14. The film of Claim 13 wherein the propylene-ethylene  
21 copolymer comprises about 1 to about 5 weight percent  
22 ethylene.

23

24 15. The film of Claim 13 wherein the propylene-ethylene  
25 copolymer comprises about 2 to about 2.5 weight percent  
26 ethylene.

27

28 16. The film of Claim 13 wherein the propylene-ethylene  
29 copolymer comprises about 2.2 weight percent ethylene.

30

31 17. The film of Claim 13 wherein the ethylene-alkyl acrylate  
32 copolymer comprises about 20 to about 25 weight percent  
33 alkyl acrylate, and the percent by weight of alkyl

34

01 acrylate based on the weight of A and B is at least  
02 about 15.

03

04 18. The film of Claim 13 wherein the ethylene-alkyl acrylate  
05 copolymer comprises about 25 weight percent alkyl  
06 acrylate, and the percent by weight of alkyl acrylate  
07 based on the weight of A and B is at least about 10.

08

09 19. The film of Claim 13 wherein the ethylene-alkyl acrylate  
10 copolymer is an ethylene-methyl acrylate copolymer.

11

12 20. The film of Claim 15 wherein the ethylene-alkyl acrylate  
13 copolymer is an ethylene-methyl acrylate copolymer.

14

15 21. The film of Claim 17 wherein the ethylene-alkyl acrylate  
16 copolymer is an ethylene-methyl acrylate copolymer.

17

18 22. The film of Claim 18 wherein the ethylene-alkyl acrylate  
19 copolymer is an ethylene-methyl acrylate copolymer.

20

21 23. The film of Claim 13 wherein the ethylene-alkyl acrylate  
22 copolymer has an average melt-point temperature equal to  
23 or greater than the value obtained from the expression:

24

25 
$$\text{temperature (deg F)} = 238 - 2.16X$$

26

27 wherein X is the alkyl acrylate content of the ethylene-  
28 alkyl acrylate copolymer.

29

30 24. The film of Claim 23 wherein the ethylene-alkyl acrylate  
31 copolymer is an ethylene-methyl acrylate copolymer  
32 having an average melt-point temperature equal to or  
33 greater than the value obtained from the expression:

34

- 25 -

01           temperature (deg F) = 248 - 2.9Y

02

03           wherein Y is the methyl acrylate content of the  
04 ethylene-methyl acrylate copolymer.

05

06

07

08

09

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 93/11456

## A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C08L 23/16, C08L 23/08, C08L 33/08  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE, A1, 2733470 (BASF AG), 15 February 1979 (15.02.79) --	1,13
A	US, A, 3555110 (R. L. MCCONNELL ET AL), 12 January 1971 (12.01.71). --	1,13
A	US, A, 4234656 (A AMEMBAL ET AL), 18 November 1980 (18.11.80) -- -----	1



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*B\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

\*G\* document member of the same patent family

Date of the actual completion of the international search

7 March 1994

Date of mailing of the international search report

25.03.94

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 5818 Patentlaan 2  
NL-2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl  
Fax (+31-70) 340-3016

Authorized officer

JACK HEDLUND

# INTERNATIONAL SEARCH REPORT

SA 2867

Information on patent family members

28/01/94

International application No.

PCT/US 93/11456

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A1- 2733470	15/02/79	NONE	
US-A- 3555110	12/01/71	NONE	
US-A- 4234656	18/11/80	CA-A- 1121543	06/04/82
		EP-A- 0013084	09/07/80
		JP-A- 55084339	25/06/80

**THIS PAGE BLANK (USPTO)**